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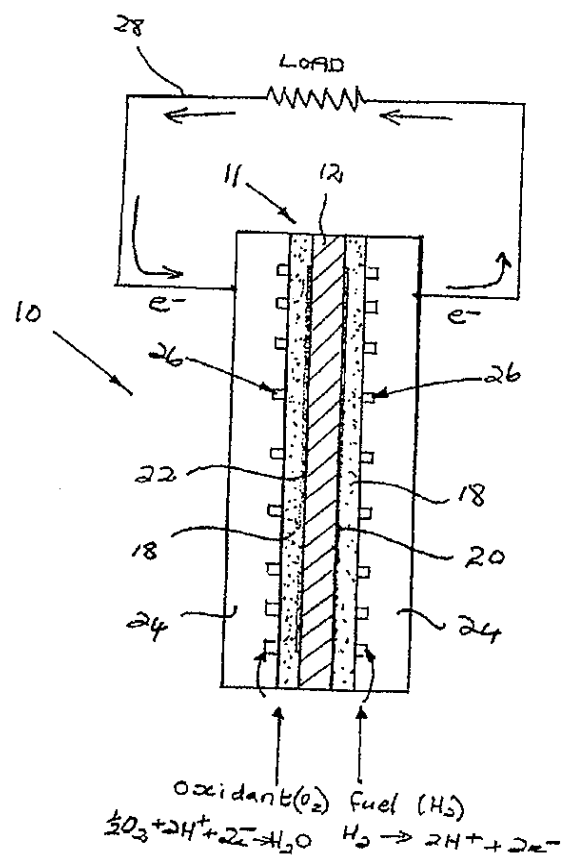
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(54) **ASSEMBLAGE D'ELECTRODES POUR COMPATIMENT DE  
RESERVOIR CHARGE DE POLYMERES HYDROPHOBES**

(54) **FUEL CELL ELECTRODE ASSEMBLY WITH HYDROPHOBIC  
POLYMER LOADING**



(57) A hydrophobic porous electrically conductive material comprises a porous electrically conductive sheet material and a hydrophobic polymer, such as polytetra-fluoroethylene, impregnated in the sheet material. The ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight and preferably about 4% to about 8% by weight. The most preferred value is about 6% of polytetrafluoroethylene to carbon sheet material by weight. In another embodiment, the polytetrafluoroethylene loading on the electrode acting as an anode is at least about two times higher than for the cathode.



**FUEL CELL ELECTRODE ASSEMBLY  
WITH HYDROPHOBIC POLYMER LOADING**

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FIELD OF THE INVENTION

This invention relates to a solid electrolyte type fuel cell, a membrane electrode assembly and a porous electrically conductive sheet material suitable for use in an electrochemical fuel cell.

BACKGROUND OF THE INVENTION

Solid electrolyte type fuel cells are known which use hydrogen gas as a fuel and an oxidant, such as oxygen gas or air. The electrolyte comprises an ion exchange membrane which is located between an anode and a cathode. The fuel gas is fed to the anode where it is oxidized to hydrogen ions with the release of electrons. The oxidant is fed to the cathode where it is reduced to form water.

The hydrogen ions and electrons produced at the anode pass through the ion exchange membrane and an external electrical circuit, respectively, to reach the cathode where they are consumed in the reduction process. The electrons flowing in the external circuit represent the usable electrical energy produced by the fuel cell.

The water formed by the reduction process at the cathode, although being an environmentally friendly and otherwise very desirable combustion product, does create problems regarding the efficiency of operation of the fuel cell in that it can accumulate on the cathode and thus "flood" the cathode. This will interfere with the oxidant reaching and coming into contact with the cathode. It has

been found that the anode is far less sensitive to hydrophobic polymer, namely TEFLON<sup>TM</sup> brand polytetrafluoroethylene, loading than the cathode and that a higher degree of polytetrafluoroethylene loading can be employed on the anode without impairing cell efficiency to strengthen the carbon fibre paper to more effectively support the membrane.

#### SUMMARY OF THE INVENTION

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It is accordingly an object of the invention to provide a hydrophobic porous electrically conductive material having a low loading of a hydrophobic polymer for use as an electrode support, particularly the cathode, and current collector to improve performance of a membrane electrode assembly in an electrochemical fuel cell.

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It is a further object of the invention to provide a membrane electrode assembly having a higher polytetrafluoroethylene loading on the anode than on the cathode for use in a fuel cell.

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According to the invention, there is provided a hydrophobic porous electrically conductive material comprising a porous electrically conductive sheet material and a hydrophobic polymer impregnated in said sheet material, wherein the ratio of the hydrophobic polymer to the sheet material is in the range of 2% to 14% by weight. The ratio is preferably in the range of 4% to 8% by weight, and most preferably about 6% by weight. The preferred hydrophobic polymer is polytetrafluoroethylene.

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Also according to the invention, there is provided a composite electrode, comprising a porous conductive sheet material having a catalytic material

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deposited thereon for operation as an electrode and a hydrophobic polymer impregnated in said sheet material, wherein the ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight. The range of hydrophobic polymer is preferably about 4% to about 8% and most preferably about 6% by weight.

Further according to the invention, there is provided a membrane electrode assembly comprising an anode, a cathode and an ion exchange membrane electrolyte interposed between the anode and the cathode, wherein the cathode is a composite electrode as described above.

According to another embodiment of the invention, there is provided a membrane electrode assembly comprising an ion exchange membrane electrolyte interposed between a pair of sheets of a porous electrically conductive material, wherein the sheets are in contact with the opposite sides of the ion exchange membrane to support the membrane, the porous sheets each having a catalytic material deposited thereon for operation as a cathode and an anode, respectively, the porous sheets each being impregnated with a hydrophobic polymer and wherein the ratio by weight of the hydrophobic polymer to the sheet material is greater on the anode than on the cathode.

Further objects and advantages of the invention will become apparent from the description of a preferred embodiment of the invention below.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The invention will now be described by way of an example, with reference to the accompanying drawings, in which:

10 Figure 1 is a schematical representation of a cross-section of an electrochemical fuel cell according to the invention;

Figure 2 is a graph showing voltage as a function of percentage polytetrafluoroethylene loading of a carbon fibre paper at different electrical currents;

15 Figure 3 is a graph showing power output of a fuel cell as a function of percentage polytetrafluoroethylene loading at different electrical currents; and

20 Figure 4 is a graph showing voltage as a function of current density for different polytetrafluoroethylene loadings on the cathode and anode.

DETAILED DESCRIPTION OF THE DRAWINGS

25 With reference to Figure 1, a cross-section through a fuel cell 10 incorporating a membrane electrode assembly 11 according to the invention is shown. The membrane electrode assembly 11 comprises a solid  
30 electrolyte in the form of a fluid impervious ion transporting membrane 12 sandwiched between a pair of carbon fibre paper sheets 18. A membrane that has been found suitable for this application is a perfluorosulfonic acid membrane such as marketed as NAFION<sup>TM</sup> by the DuPont  
35 company or a membrane marketed as XUS 13204.10 by the Dow company.

The membrane may have a thickness ranging from 0.0035 inches or less, to about 0.01 inches, but it has been found that a thinner membrane improves fuel cell efficiency significantly.

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Each sheet of carbon fibre paper 18 is provided with a coating of catalytic material for operation as an anode 20 and a cathode 22, respectively. An electrically conductive endplate 24 is provided against the outside of each sheet of carbon fibre paper 18 to complete the fuel cell 10.

Although the fuel cell 10 illustrated in the present example comprises only one membrane electrode assembly 11, it will be appreciated that the fuel cell 10 can comprise a plurality of membrane electrode assemblies 11 connected in series with suitable separator plates between adjacent membrane electrode assemblies 11.

The endplates 24 are each provided with a maze of grooves 26 for feeding the fuel and oxidant gases to the anode and cathode respectively and they also serve as passageways for the removal of water from the cathode 22. The endplates 24 further serve as the connections to an external electrical circuit 28 through which the electrons flow, as indicated by the arrows.

The carbon fibre paper 18 is impregnated with a hydrophobic polymer, such as TEFLON™ (polytetrafluoroethylene), to render the carbon fibre paper 18 hydrophobic as well as to provide mechanical strength thereto so that it can act as a proper support for the membrane 12 sandwiched between the sheets of carbon fibre paper 18. A carbon fibre paper which has been found to be suitable for the present application is the product

commercially supplied under the name "TGP" by Toray and in particular the sheet having a thickness of 0.27 mm and designated "TGP-90". However, it will be appreciated that other carbon fibre papers can also be used, such as PC206 from Stockpole Corporation or KGF-200 by Kureha. The thickness of the carbon fibre paper may be in the range of 0.1 mm to 0.45 mm and preferably about 0.3 mm. The carbon fibre paper has a bulk density in the range of about 0.25 g/cm<sup>3</sup> to about 0.60 g/cm<sup>3</sup>.

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The polytetrafluoroethylene is provided as a slurry in water and typically includes a dispersing agent. A product by DuPont which is commercially available under the name TEFLON™ 30B TFE resin dispersion has been found to be a suitable product for use as the hydrophobic polymer. The dispersion comprises negatively charged hydrophobic colloid containing TFE resin particles suspended in water and stabilized with a non-ionic wetting agent.

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An example of the method of impregnation of the carbon fibre paper with polytetrafluoroethylene is given in Example 1 below.

#### Example 1

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#### Impregnation with polytetrafluoroethylene

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3.5 ml TEFLON™ 30B was added to 95 ml water. The water and TEFLON™ were mixed to form a slurry. A sheet of carbon fibre paper (TGP-90) 0.27 mm thick and weighing 3.0015 g was soaked in the slurry for about 10 to 15 minutes. The carbon fibre paper was then air dried for 10 to 15 minutes. The carbon fibre paper was sintered on the surface of a hotplate at a temperature of from about 350°C. to 410°C. for 10 to 15 seconds. The resulting

wet-proofed carbon fibre paper had a mass of 3.1924 g. Accordingly, the amount of TEFLON™ added was .01909 g, i.e. the ratio of TEFLON™ to carbon fibre paper was 5.98% by weight.

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An example of a method of providing a coating of catalytic material on the carbon fibre paper is given in Example 2 below.

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Example 2

Coating with catalytic material

18 ml of TEFLON™ 30B was added to 82 ml of water. The water and TEFLON™ were mixed to form a slurry. 0.4 ml of the slurry, 929.0 mg of finely divided platinum and 20 droplets of 1.0 N sulphuric acid were placed on one side of the sheet of carbon fibre paper treated according to Example 1. The components were mixed with a spatula and spread evenly over the surface of the carbon fibre paper. After air drying for about two hours, the carbon fibre paper was sintered for about 30 seconds on the surface of a hotplate at about 410°C.

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An example of the formation of a membrane electrode assembly is given in Example 3 below.

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Example 3

Membrane electrode assembly

A DOW XUS 13204.10 ion exchange membrane was soaked in 2 M sulphuric acid for 48 hours. The membrane was then rinsed twice with deionized water and boiled in water having a pH of 5 for about one hour. Thereafter, the membrane was again rinsed twice in deionized water.

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Two pieces of sheet metal were each covered with a piece of aluminum foil. One sheet of TEFLON™ impregnated carbon fibre paper was placed on the one sheet with the side having the coating of electrode material facing upwards. The membrane was then placed on top of the sheet of carbon fibre paper. Another sheet of carbon fibre paper, which was also impregnated with TEFLON™ and provided with a coating of catalytic material, was placed on the membrane with the side coated with the electrode material facing the membrane. The second piece of sheet metal was placed over the top sheet of carbon fibre paper with the aluminum foil facing the carbon fibre paper. The sheet metal assembly was then placed in a heated press between platens which were maintained at about 175°C. The platens were closed and a pressure of 1000 psi was applied for about four minutes. The assembly was then removed from the press. The sheet metal plates were separated, leaving the aluminum foil adhering to the membrane electrode assembly. The foil was peeled off to expose the bonded membrane electrode assembly laminate which was stored in water in a plastic bag until required for use.

Further membrane electrode assemblies were prepared according to the method described in the examples above, but varying the amount of TEFLON™ in the carbon fibre paper. The membrane electrode assemblies were incorporated in fuel cells and the voltage was measured at different currents. The results are tabulated in Table I.

TABLE I

	<u>% TEFLON™</u>	<u>CURRENT (A)</u>	<u>VOLTAGE (V)</u>	<u>POWER (W)</u>
5	2.4	250	0.561	140.25
		275	0.529	145.48
		300	0.478	143.4
		325	0.438	142.35
10	4.1	250	0.636	159.0
		275	0.608	167.2
		300	0.576	172.8
		325	0.533	173.23
15	6.0	250	0.645	161.25
		275	0.618	169.95
		300	0.584	175.2
		325	0.548	178.1
20	10.3	250	0.614	153.5
		275	0.586	161.15
		300	0.543	162.9
		325	0.481	156.33
25	11.1	250	0.605	151.25
		275	0.562	154.55
		300	0.502	150.6
		325	---	---
30	14.3	250	0.526	131.5
		275	0.472	129.8
		300	0.427	128.1
		325	0.383	124.48
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The voltages measured are graphically illustrated as a function of percentage TEFLON™ loading at the different current densities in Figure 2. The percentages given are for the ratio of TEFLON™ to carbon fibre paper by weight. It is clear from this figure that better values for the voltage are obtained in the range of about 2% to about 14% TEFLON™ loading. The best results are obtained at a loading of from about 4% to about 8% and an optimum value is at about 6% TEFLON™ loading.

In Figure 3, the power delivered is graphically illustrated as a function of percentage TEFLON™ loading for the four currents tested. This Figure also shows that better power output is obtained with TEFLON™ loadings in the range of about 2% to 14% with the best values being obtained at a TEFLON™ loading of from about 4% to about 8% and an optimum value appearing to be about 6%.

In Figure 4, voltage is graphically illustrated as a function of current density for membrane electrode assemblies having different TEFLON™ loadings on the anode and cathode respectively, as shown by the data given in the drawing.

It is clear from the graph that, whereas there is a marked drop in voltage as the TEFLON™ loading on the cathode departs from the optimum value of about 6%, there is no such sensitivity for the TEFLON™ loading on the anode.

Accordingly, the TEFLON™ loading on the anode can be raised without detrimental effect on cell efficiency, preferably at least about two times the loading on the cathode, in cases where additional strengthening support for the ion exchange membrane is required, particularly where very thin membranes are

employed. This, therefore allows membrane electrode  
assemblies to be constructed with thin membranes to obtain  
maximum cell efficiency, but still providing sufficient  
strength for the membrane assembly due to the increased  
5 TEFLON™ loading on the anode.

While only preferred embodiments of the  
invention have been described herein in detail, the  
invention is not limited thereby and modifications can be  
10 made within the scope of the attached claims.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A hydrophobic porous electrically conductive material  
sintable for use in an electrochemical fuel cell,  
comprising:  
  
a porous electrically conductive sheet material; and  
  
a hydrophobic polymer impregnated in said sheet  
material,  
  
wherein the ratio of the hydrophobic polymer to the  
sheet material is in the range of about 2% to about  
14% by weight.
2. The hydrophobic material according to claim 1,  
wherein said ratio is in the range of about 4% to  
about 8% by weight.
3. The hydrophobic material according to claim 2,  
wherein said ratio is about 6% by weight.
4. The hydrophobic material according to claim 1,  
wherein said polymer is polytetrafluoroethylene.
5. The hydrophobic material according to claim 1,  
wherein said sheet material is carbon fibre paper.
6. The hydrophobic material according to claim 5,  
wherein the thickness of said carbon fibre paper is  
in the range of about 0.1 mm to about 0.45 mm.
7. The hydrophobic material according to claim 5,  
wherein said carbon fibre paper has a porosity of in  
the range of about 70% to about 80%.

8. The hydrophobic material according to claim 5, wherein said carbon fibre paper has a bulk density in the range of about  $0.25 \text{ g/cm}^3$  to about  $0.60 \text{ g/cm}^3$ .
9. A composite electrode for use in an electrochemical fuel cell, comprising:  
  
a porous electrically conductive sheet material having a catalytic material deposited thereon for operation as an electrode; and  
  
a hydrophobic polymer impregnated in said sheet material, wherein the ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight.
10. The composite electrode according to claim 9, wherein said catalytic material is deposited on one surface thereof.
11. The composite electrode according to claim 10, wherein said catalytic material comprises a finely divided platinum group metal and a polymeric binder.
12. The composite electrode according to claim 11, wherein said platinum group metal is platinum.
13. The composite electrode according to claim 11, wherein said polymeric binder comprises polytetrafluoroethylene.
14. The composite electrode according to claim 9, wherein the ratio of said hydrophobic polymer to said sheet material is in the range of about 4% to about 8% by weight.

15. The composite electrode according to claim 14, wherein said ratio is about 6% by weight.
16. The composite electrode according to claim 9, wherein said hydrophobic polymer comprises polytetrafluoroethylene.
17. The composite electrode according to claim 9, wherein said sheet material comprises carbon fibre paper.
18. A membrane electrode assembly comprising:
  - an anode;
  - a cathode; and
  - an ion exchange membrane electrolyte interposed between said anode and said cathode,wherein said cathode comprises:
  - a porous electrically conductive sheet material having a catalytic material deposited thereon for operation as an electrode; and
  - a hydrophobic polymer impregnated in said sheet material;wherein the ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight.
19. The membrane electrode assembly according to claim 18, wherein the ratio of said hydrophobic polymer to said sheet material is in the range of about 4% to about 8% by weight.

20. The membrane electrode assembly according to claim 19, wherein said ratio is about 6% by weight.
21. The membrane electrode assembly according to claim 18, wherein said polymer is polytetrafluoroethylene.
22. The membrane electrode assembly according to claim 18, wherein said paper is carbon fibre paper.
23. The membrane electrode assembly according to claim 18, wherein the thickness of said carbon fibre paper is in the range of about 0.1 mm to about 0.45 mm.
24. The membrane electrode assembly according to claim 18, wherein said carbon fibre paper has a porosity in the range of about 70% to about 80%.
25. The membrane electrode assembly according to claim 18, wherein said carbon fibre paper has a bulk density in the range of about 0.25 g/cm<sup>3</sup> to 0.60 g/cm<sup>3</sup>.
26. The membrane electrode assembly according to claim 18, wherein said anode comprises:
  - a porous electrically conductive sheet material having a catalytic material deposited thereon for operation as an electrode; and
  - a hydrophobic polymer impregnated in said sheet material;wherein the ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight.



27. A membrane electrode assembly comprising an ion exchange membrane electrolyte interposed between a pair of sheets of a porous electrically conductive material, wherein said sheets are in contact with the opposite sides of the ion exchange membrane to support said membrane, said porous sheets each having a catalytic material deposited on a surface thereof for operation as a cathode and an anode, respectively, said porous sheets each being impregnated with a hydrophobic polymer and wherein the ratio by weight of said hydrophobic polymer to said sheet material is greater on the anode than on the cathode.
28. The membrane electrode assembly according to claim 27, wherein the ratio of said hydrophobic polymer to said sheet material on the cathode is in the range of about 2% to about 14% by weight.
29. The membrane electrode assembly according to claim 28, wherein said ratio is in the range of about 4% to about 8% by weight.
30. The membrane electrode assembly according to claim 29, wherein said ratio is about 6% by weight.
31. The membrane electrode assembly according to claim 27, wherein the ratio by weight of said hydrophobic polymer to said sheet material on the anode is at least about two times said ratio for the cathode.
32. An electrochemical fuel cell comprising a membrane electrode assembly comprising:  
  
an anode;

a cathode; and

an ion exchange membrane electrolyte interposed  
between said anode and said cathode,

wherein said cathode is a composite electrode  
comprising;

a porous electrically conductive sheet material  
having a catalytic material deposited on a surface  
thereof for operation as an electrode; and

a hydrophobic polymer impregnated in said sheet  
material;

wherein the ratio of the hydrophobic polymer to the  
sheet material is in the range of about 2% to about  
14% by weight.

33. The electrochemical fuel cell according to claim 32,  
wherein said anode comprises:

a porous electrically conductive sheet material  
having a catalytic material deposited thereon for  
operation as an electrode; and

a hydrophobic polymer impregnated in said sheet  
material;

wherein the ratio of the hydrophobic polymer to the  
sheet material is in the range of about 2% to about  
14% by weight.

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FUEL CELL ELECTRODE ASSEMBLY  
WITH HYDROPHOBIC POLYMER LOADING

ABSTRACT OF THE DISCLOSURE

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A hydrophobic porous electrically conductive material comprises a porous electrically conductive sheet material and a hydrophobic polymer, such as polytetrafluoroethylene, impregnated in the sheet material. The ratio of the hydrophobic polymer to the sheet material is in the range of about 2% to about 14% by weight and preferably about 4% to about 8% by weight. The most preferred value is about 6% of polytetrafluoroethylene to carbon sheet material by weight. In another embodiment, the polytetrafluoroethylene loading on the electrode acting as an anode is at least about two times higher than for the cathode.

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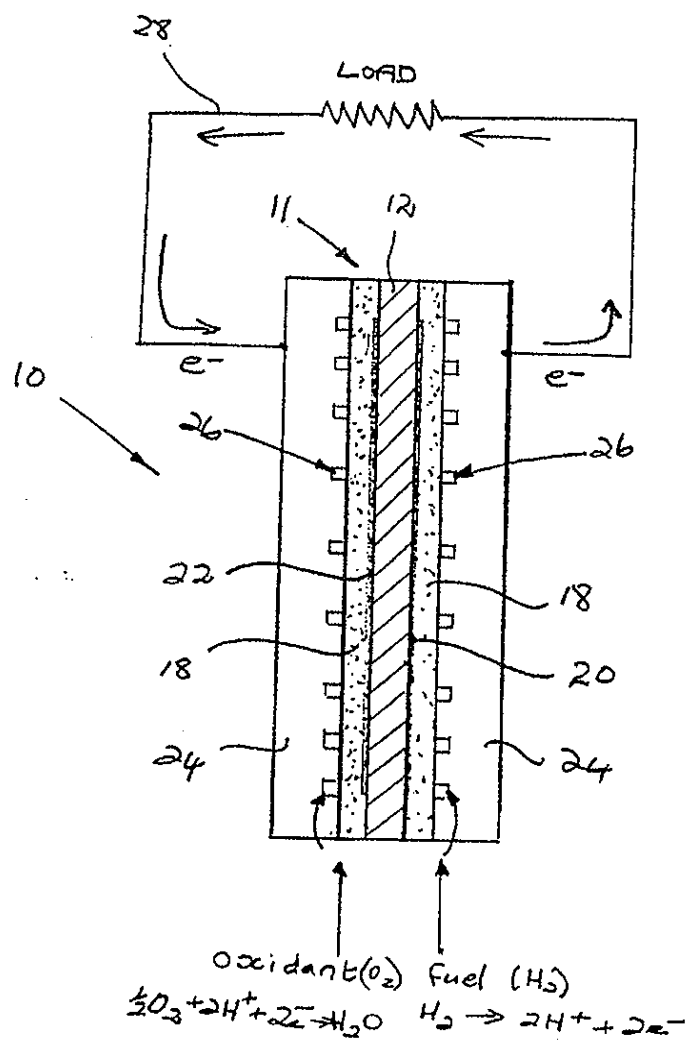


Fig 1

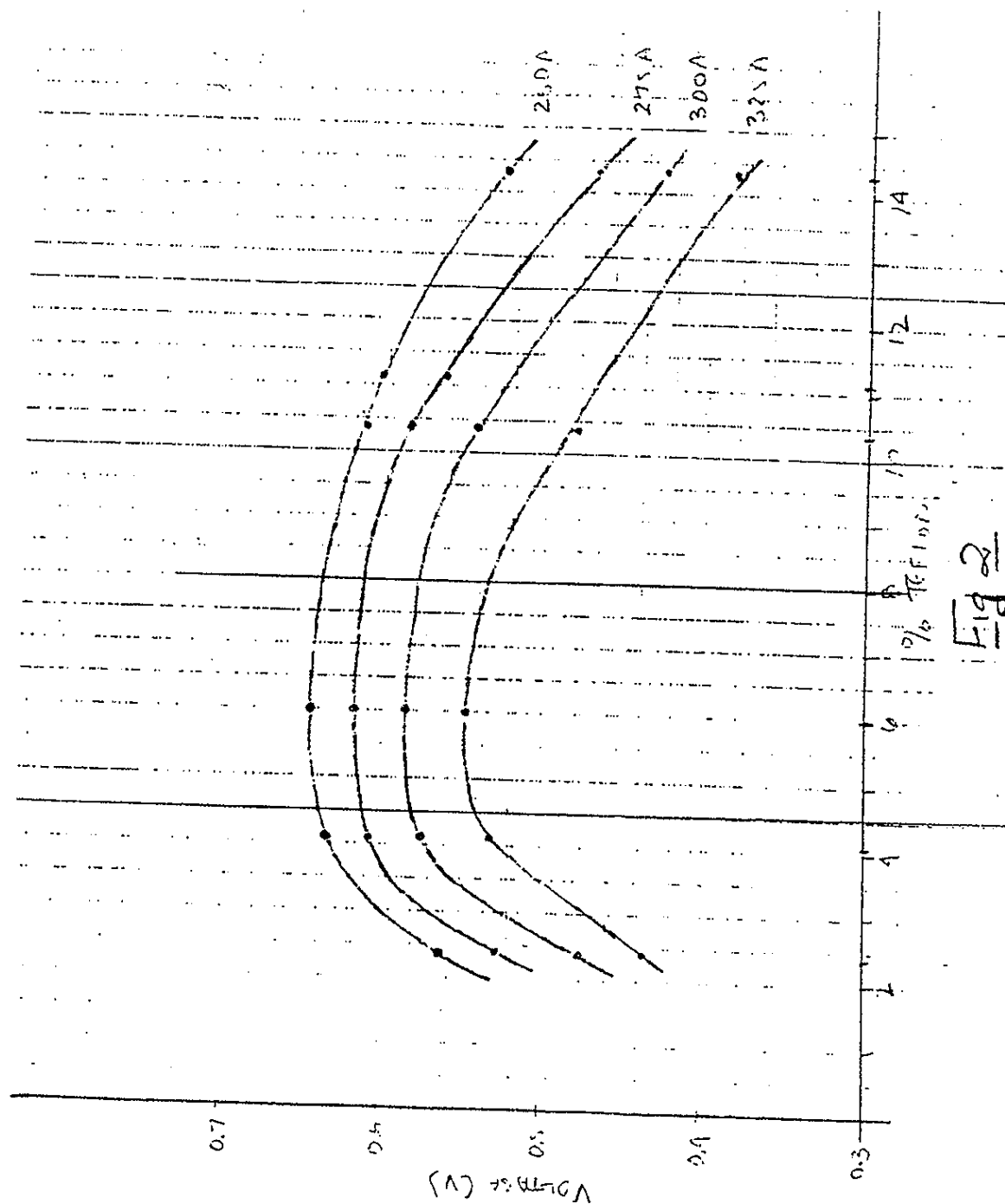
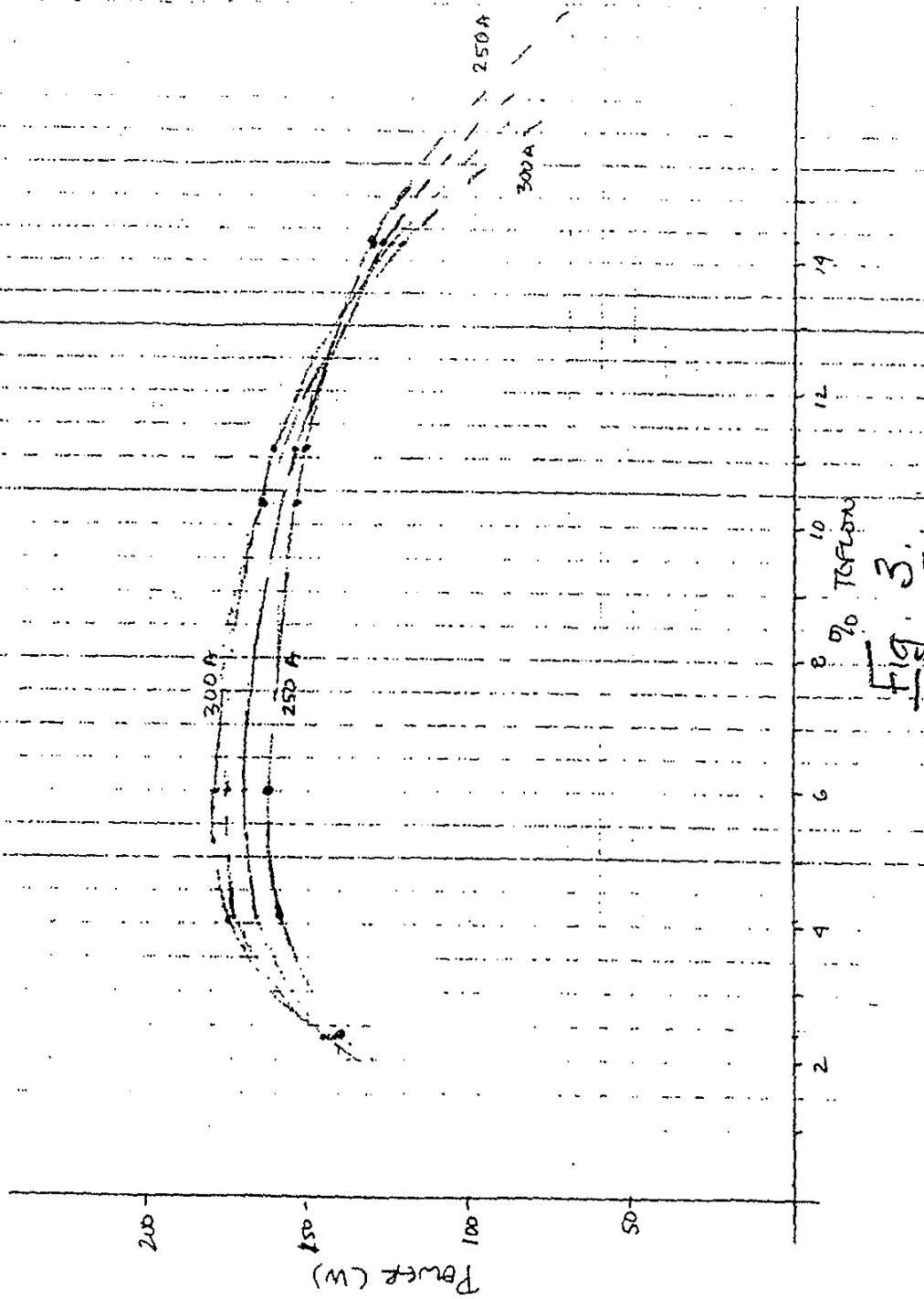


Fig 2



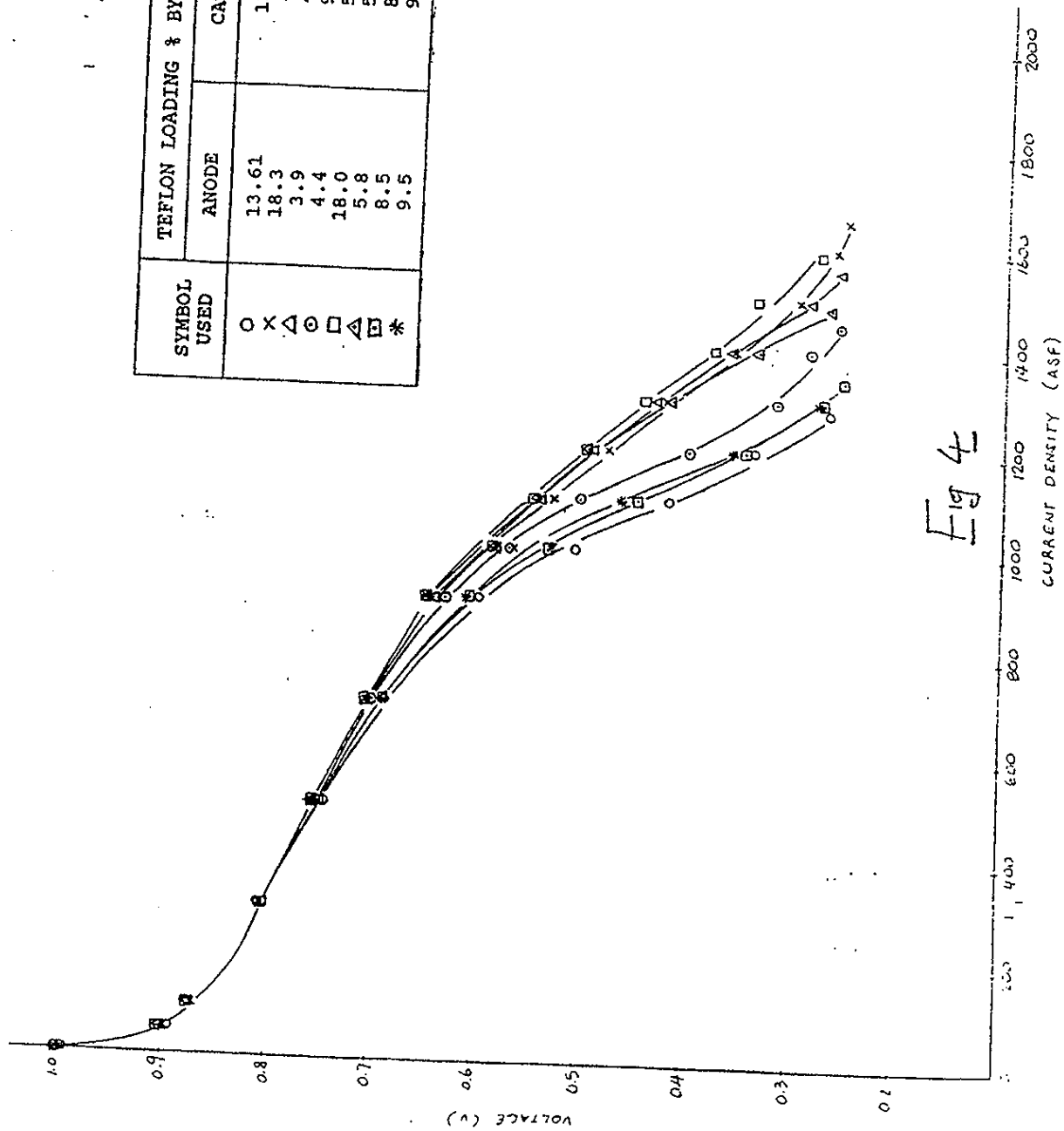


Fig 4